

Review

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RECOVERY OF METALLIC COPPER FROM ACID LEACH SOLUTION Part I

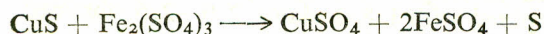
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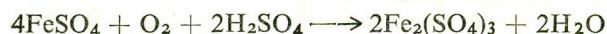
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INTRODUCTION

The leaching of copper minerals results invariably in acidic solutions except in cases where ammonia-ammonium carbonate mixture [1],* alkali cyanides [2,3] or caustic alkalis [4] are used depending on the nature of host rock. Solutions of sulphuric acid are the most commonly used leaching agents for oxidised copper minerals.† In the presence of small quantities of sulphide minerals like pyrite, chalcopyrite, the presence of ferric sulphate is necessary:



The ferric sulphate needed for the leaching of minerals is produced during the reaction in the presence of dissolved oxygen.



Or it may also result as a product of oxydation of ferrous iron present in acid solutions, or of sulphur, metal sulphides or lower oxyacids of sulphur by specific strains of bacteria.

Since most of world's copper occurs in sulphide form, with an overburden of oxidised ore, and the conventional method of smelting has been a cause of atmospheric pollution, great attention has been given to the hydrometallurgical treatment of sulphides. It is not the purpose of this review to treat the methods of leaching of copper ores. However, a selected bibliography [5-19] on different leaching procedures has been presented.

The discovery of copper ore at Saindak in Pakistan [20] and later laboratory studies [21] on the leaching behaviour of this ore have prompted this work and it is hoped that literature cited here will be of some interest and help to the people engaged on this project.

* For chemistry of dissolution see : A.R. Berkin, *The Chemistry of Hydrometallurgical Processes*. (E. and F.N. Spon, London, 1966).

† Butts, *Copper, the Metal, its Alloys and Compounds* (Reinhold, New York).

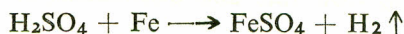
METHODS OF METAL EXTRACTION

The solutions of copper sulphate obtained from different leaching operations differ in copper content and acidity. For example, the leach solution from a predominantly oxidised ore leached in vats by percolation or agitation will contain more copper values than that obtained from leaching of a tailing dump. In general these solutions are said to contain copper from 1-3 g/l at a pH of 0.5-2.5 [22]. Metallic copper is recovered from these solutions by the methods described below.

I. Cementation

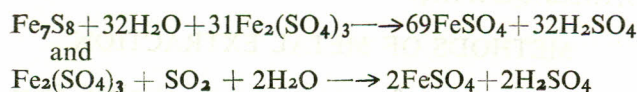
This is the oldest method of recovering copper from solutions (e.g. mine waters). The chemistry of the process has been known for centuries, however, the method came into commercial use as early as 1752 [23]. The precipitation is carried out in launders, cementation cells or precipitation cells by lighter iron sheet scrap followed by tin cans. The precipitated copper powder is collected in separate settling tanks and the ferrous sulphate solution is either aerated to precipitate basic ferric sulphate (which after roasting may be sold as red pigment) or allowed to crystallise as ferrous sulphate. The cement copper is usually between 80-90% pure. The common impurities encountered are silica, iron, alumina, ordinary silt and oxides of copper [24]. Free iron particles are removed by magnetic separation while other impurities by froth floatation. Alternately the contaminated cement copper is sent to reverberatory furnaces where it is smelted to produce the so called blister copper which is around 98% pure.

During the course of cementation the following reactions have been recognised to take place [25].



First of these equations represents the real cementation reaction and indicates an iron consumption of 0.88 lb/lb of copper produced. The higher consumption of iron in practice (1.5-2.5 lb/lb Cu) is attributed to the other reactions taking place

simultaneously. Obviously the reduction of contact time between scrap and solution and reduction of ferric ion to ferrous state before cementation will result in more efficient precipitation at a lower iron consumption. Thus Taylor *et al.* [26] have reported the use of sulphure dioxide as reductant for ferric sulphate at Rio Tinto prior to cementation while Jacobi [27] has used pyrrhotite ore and sulphur dioxide from roaster gases for the same purpose and has reported an iron consumption of 1.25 lb/lb Cu produced.



Another important factor contributing to an efficient precipitation is the surface area of the scrap. In fact iron consumption is the cost controlling factor in cementation.

Therefore, in order to reduce iron consumption and obtain optimum copper recoveries many improvements in the design of cementation apparatus have been made along with the search for various forms of iron to be used. Thus automobile scrap, tin plate, sponge iron, iron powder, iron plates, particulate iron etc. have been used.

Spedden and his coworkers [28] introduced a cone-shaped cementation apparatus. The cone is filled with shredded iron through which copper-bearing solutions are pumped upwards. During operation of these cones they observed that the application of kinetic principles resulted in the production of a more granular and high purity copper cement as compared to the conventional launder process.

Hogue [29] got patented an elongated upright V-shaped trough for the precipitation of copper on sponge iron. The copper bearing solution is made to enter the vessel with force at the bottom through conduit having holes at the end, so that the sponge iron gets suspended and remains in agitated state. The copper powder deposited on iron is rubbed off and washed upwards where it is collected from the barren solution overflow in separate tanks. The collected copper contains small particles of iron as impurity.

Jacky [24] has described the precipitation of copper in launders on a mixture of 50% reclaimed and cleaned tin cans and 50% tin plate from can manufacturers. The solution coming from tank leaching of chrysocolla gives a cement containing 95% copper in a strong sponge like nodule whereas a dump leach solution produces nodules with cuprous oxide and hydrous iron oxides as contaminants. The author has also discussed the grade, contaminant control, flow rate and distribution of pregnant solutions.

Back [30] has reported the use of a prototype cone 20 ft high of 20 ft dia with a capacity of 1000 gallons of solution/min. Sponge or particulate iron obtained from the direct reduction of magnetic concentrates, iron ore or pyrite cinders has been used as precipitant. A saving of 0.5–1.0 lb Fe/lb Cu produced has been achieved as compared to the launder cementation from the same solution. Recoveries of

copper run to 95% before a bed of dynamically suspended precipitant is established, and then recoveries of more than 99% are common. Generally particulate iron of –35 mesh size is necessary but when a sponge iron or spongy product with a high specific area is used, a 10-mesh product has been found to be suitable.

Dean *et al.* [31] employed a stainless-steel rotary drum 18 in dia and 36 in long containing cleaned automobile scrap. The solution containing 1.5:1.6 and 2.5 g/l of Cu, Fe²⁺ and sulphuric acid respectively was contacted with the scrap and it was observed that the precipitation was faster and more complete than when shredded detinned tin plate scrap was used in a launder, with a comparable iron consumption: copper recovery of 92.3% has been reported.

A pulsed or unsteady state column precipitator treating 10–20 gallons/min of pregnant solution with iron in various forms has been operated by Allman and his coworkers [32]. The column was an 8 in dia by 10 ft high rubber-lined mild steel pipe expanded at its overflow. Turbulence combined with abrasion during pulsing of the precipitant bed were responsible for exposing fresh iron surface to the solution. The copper cement grades in these tests were 70–90% as compared with a conventional launder and a Kennecott cone precipitator, respectively. The iron factor (ratio of weight of iron consumed to weight of copper produced) was 1.3–2.0 compared with 1.8–2.5 and 2.0–2.5 obtained with two earlier methods.

Kennecott Copper Corporation obtained a patent [33] on the use of a 20-ft deep commercial vessel in which a 99% recovery with 1.35 lb powdered iron/lb of copper produced was possible as compared to 2.25 lb iron powder/lb copper in a launder using the same solution. Care was taken that hydrogen produced during the reaction did not escape but remained in the vessel at a partial pressure of 1.2 atmospheres. The vessel was 7 ft deep above the reaction zone and might or might not be covered.

In addition to what has been described above a number of attempts have been made in the design and development of a new precipitation apparatus with a view to minimising the consumption of iron and recovering maximum of copper at the same time. In this connection the work of Keyes [34], Zimmerley and Malouf [35], Thomas Valle [36], Golubkov *et al.* [37], Klushin *et al.* [38], Krivsky *et al.* [39], Subbelfield [40], Ransom [41], Khalezov *et al.* [42] and many others forms a valuable contribution on the subject.

In the meantime several kinetic studies have been made to follow the precipitation reaction under various experimental conditions. Thus Sarmaitis *et al.* [43] studied the effect of concentration and temperature on the ion exchange between iron and Cu²⁺ using polished and etched Armco iron plates for the precipitation of copper from sulphate solutions. According to their observations the rate of the contact exchange decreases with increase of sulphuric acid concentration in the solution from 0–100 gl. With increase in copper concentration, the rate goes

through a maximum. The parallel reaction of iron dissolution ($\text{Fe} + 2\text{H}^+ \rightarrow \text{Fe}^{2+} + \text{H}_2 \uparrow$) was found to be appreciable only in strongly acidic solutions at low Cu^{2+} concentration.

In another kinetic study Nadkarni and Wadsworth [44] found the cementation reaction to be of the first order, the rate of precipitation increasing with agitation to a limiting value. They also studied the effect of the presence in solution of ferrous and ferric ions and observed that the back reaction due to Fe^{2+} was negligible. The direct reaction of Fe^{3+} with iron is not as important as its reaction with metallic copper.

While Denny and Krishnaswami [45] found that injection of air into solution being contacted with iron was helpful in increasing the rate and degree of precipitation of copper, Miller and Beckstead [46] showed that the nature of deposit was a controlling factor in the kinetics of cementation in certain cases and determines the effective cathodic area.

From what has been said above it may easily be concluded that during the last two decades great efforts have been made to improve the technique of cementation with special stress on the recovery and purity of copper produced using minimum possible of iron per unit weight of copper obtained. As a result copper cement of 95–99% [34] purity has been obtained with recoveries running as high as 99% [33]. Also the consumption of iron has been reduced to 1.25 lb/lb of copper [27] as compared to around 2.25 lb/lb Cu in the conventional launder process.

II. Solvent Extraction or Liquid-Liquid Extraction

The recovery of copper from acid sulphate solutions by solvent extraction is comparatively a recent development. The process got impetus in 1964 when General Mills introduced LIX 64 [47] and later pilot plant testing started at Rancher's [48], Duval [49] and Bagdad Copper Corporation [50]. The solutions used were obtained from dump leaching and LIX 64 in kerosene was employed as an extractant. The progress of and the results obtained from pilot tests at Rancher's have been described in detail by Dasher and Power [48]. Besides these pilot tests there were other laboratory and pilot testing at about the same time and these have been described in another publication [51]. In fact the development in this field has been so rapid that after the first Rancher's plant in 1968, there are a number of plants running by now, some of which have been properly described in literature [52–56] (Table 1) and many others are being planned.

The process consists essentially of agitating the pregnant leach liquor with the organic solvent in a mixer settler unit, the two streams flowing counter current to each other. The mixture is then allowed to settle in a settler tank, where the two phases are separated. The loaded organic phase thus separated is sent to the stripping section where the metal is stripped with sulphuric acid regenerating the extractant. The regenerated extractant is recycled to the mixer while the barren aqueous phase

(or raffinate) from the settler is sent back to the leaching operation. The copper sulphate solution obtained from stripping operation is sent to the electrowinning section where it is electrolysed to produce the so called copper cathodes.

The extractants in current use are viscous and require dilution before use in the extraction operation. The dilution gives the extractants such properties as improved dispersion in the organic phase, improved settling characteristics and lesser tendency to form emulsions with aqueous phase. A variety of diluents have been tried (from pure aromatic to pure aliphatic) but on a commercial scale it is kerosene which is generally used. The concentration of extractant in the organic phase may vary from 2 to 50% v/v [57]. The organic phase also contains a modifier whose main function is to prevent the formation of a third phase. Such modifiers as 2-ethylhexanol, isodecanol, *p*-nonylphenol and tri-*n*-butylphosphate have been used.

At present the organic extractants used on a commercial scale come from the LIX series introduced by General Mills. The first of this series was LIX 63 [58], an aliphatic α -hydroxy oxime, which although extracted copper from leach liquors, was neither selective for copper in presence of ferric iron (invariably always present in leach liquors and a nuisance in the electrowinning operation) nor worked in the pH range of the leach liquors LIX 64 [59] was the next to come. Based on β -hydroxybenzophenone oxime structure, this extractant has both the selectivity and pH functionality; thus it was the first to be used on commercial scale. The research workers at General Mills then developed LIX 65 N, an alkyl β -hydroxybenzophenone. Later work showed that if LIX 63 be added to LIX 65 N, the phase separation is improved and better temperature functionality is obtained. The LIX 63 and LIX 65 N mixture was given the name of LIX 64 N [60]. This extractant had such improved performance for copper extraction from dump leach solutions at their natural pH that such a large unit was based on it. The LIX reagents enterprise as NCCM's Chingola Copper recovery i.e. LIX 64, LIX 65 N, LIX 64 N) have proved to be efficient for copper extraction from such solutions as come from heap leaching, tailings dumps leaching, natural mine waters etc. and contain not more than 5 g/l of copper in any case at a pH in the range of 1.0–2.0 (sometimes even less than 1.0). With the rapid disappearance of these and similar sources and in the face of campaigns from environmentalists for pollution-free atmosphere, the trend in copper industry has been towards hydrometallurgical preparation of solutions from high grade oxide ores (where they are available, as in Pakistan) and sulphide ores or concentrates. The solutions may contain copper values as high as 40 g/l [62] and 80 g/l [63]. For the extraction of copper from such solutions, the General Mills introduced LIX 70 [64]. This reagent was capable of extracting copper from solutions containing up to 60 g Cu/l or equilibrium sulphuric acid concentrations of 100 g/l. The excellent extraction and pH functionality of this reagent

is, however, attained at the cost of stripping efficiency where sulphuric acid up to 300 g/l is required. With a view to increase the net transfer and stripping efficiencies two new LIX reagents were introduced: LIX 71 and LIX 73. Agers and De Ment [65] have described the evaluation procedures for these reagents in particular practical cases. They have also made suggestions for the design of commercial mixer-settler units whereas Atwood and Miller [66] have established the structure of LIX reagents and Kelex-100 based on their analytical studies and have found stoichiometry of the reactions of extraction to be as follows:



The LIX reagents can extract copper not only from acid solutions but they have been proved useful for copper recovery from ammoniacal solutions. Thus a patent has been awarded to Stern *et al.* [67] for the extraction of copper containing zinc with a hydroxy oxime in kerosene used as extractant. Ritcey and Lucas [68] have studied the separation of copper from Ni and Co from an ammoniacal solution using LIX 63. They have also compared the cost of SX—EW with hydrogen sulphide precipitation of copper followed by smelting. They have proposed a flow sheet for the recovery and separation of Ni, Co and Cu from ammonia leach liquors resulting from ammonia pressure leaching of Ni-sulphide concentrates. With the recent introduction of Arbiter ammoniacal leaching of copper sulphide concentrates [69] at atmospheric pressure, the scope of hydrometallurgy of sulphidic copper ores has enhanced. The copper values are recovered by LIX extraction and the ammonium sulphate in the raffinate may be either recovered and used as fertilizer or limed to form gypsum recovering ammonia at the same time with steam. The one inconvenience in LIX extraction of copper from ammoniacal solutions is the solubility of ammonia in the organic phase. This problem may, however, be overcome by slightly acidic water washing of the loaded organic phase or a sodium sulphate washing at elevated temperature [70].

Another series of reagents with comparable extraction characteristics comprises of Kelex 100 and 120. Kelex 100 [71] is a substituted 8-hydroxyquinoline whereas Kelex 120 is its modification obtained by dissolving it in nonylphenol [72]. A patent by Budde and Hartlage [73] describes the use of substituted 8-hydroxyquinolines for the extraction of copper from dilute CuSO_4 dump leach liquors and from solutions containing vanadium values. The reagents have been claimed to have excellent extraction properties, loading capacities and pH functionality. Ritcey [74] has studied the extraction of copper from acidic solutions, resulting from leaching of copper concentrates, with Kelex 100. The extraction of copper has been studied as a function of time, temperature, equilibrium, choice of modifier, stripping characteristics etc. and an estimate of processing cost of particular acidic leach solution, containing iron, nickel and traces of cobalt

has been presented. In another publication Ritcey and Lucas [62] have studied the variables affecting the coextraction of iron in a copper circuit, soluble solvent losses in the acidic range, use of the extractant Kelex 100 for metals other than copper, stagewise extraction at a controlled pH, stripping problems and compatibility with LIX 64 N. Atwood and Miller [66] have published the comparative extraction data for Kelex 100, LIX 70, 64 N, 64 and 63 which shows that Kelex 100 is an even stronger extractant than LIX 70. Hartlage [75] has described extraction properties of Kelex 100 in detail. Kelex 120 being already a solution of Kelex 100 in nonylphenol, does not require a third phase inhibitor in the organic phase. Because of higher extraction capacity and better stripping characteristics, the Kelex reagents can handle both dilute and relatively concentrated copper solutions. Other chemical and physical factors to be evaluated before designing Kelex extraction system have been discussed by Hartlage and Cronberg [76] and briefly dealt with by Flett [77].

A number [18,68,77,78,79] of cost comparisons have been made between the conventional cementation-smelting method and the solvent extraction process and it has been established beyond doubt that solvent extraction is a better process not only economically but also technically. At the same time the SX process has its own problems, the most talked about being the solvent loss in view of its high cost. The solvent loss results generally due to its entrainment with the aqueous phase. It has, however, been proved from commercial experience that total solvent loss of less than 0.5 gallons (50 ppm)/1000 gallons of aqueous treated can be achieved with proper mixer-settler design [65]. Accordingly to another study the loss of Kelex 100 is of the order of 10 ppm at pH 0.5 and less than 1 ppm in the pH range of 1.5–6.0 [62]. To reduce further the solvent losses and to avoid any pollution of effluent streams, Ashbrook [57] has stressed the need of improved, quick and easily operable methods of analysis at the plant. In his publication he has discussed at length the available methods of analysis for different types of extractants usually encountered in solvent extraction processes. In a beautiful article Kindig and Hazen [80] have shown that the use of cyclones for phase separation could be fruitful if a diluent of higher specific gravity than kerosene is used. They have used perchloroethylene and by operating their cyclone system over a long period of time continuously they found that the discharged aqueous solution contained only 0.042 vol % of organic. Another problem is the contamination of copper cathode by lead which originates from the lead-antimony anodes used in the electrowinning plant and ranges from 10 to 100 ppm whereas tolerable limit has been said to be less than 10 ppm. To alleviate this situation titanium anodes coated with precious metals have been proposed. The production of a purer electrolyte through solvent extraction permits the operation of electrowinning plant at higher current densities (of the order of 600 A/m²). The production of acid mists in the tank house is bound to result for which

no perfect answer has been found although Agers [65] has touched upon this subject in his publication.

Besides the LIX and Kelex extractants there are others (Table 2) which have been used for the extraction and separation of copper in the presence of other metals. Among these are encountered the phosphoric acids and phosphates, carboxylic acids, naphthenic acid and naphthenates, sulphonic acid and sulphonates; long chain amines and quaternary amine halides etc. From among the phosphoric acids di-(2-ethylhexyl)phosphoric acid [81-86] has found extensive use as an extractant. It is manufactured by Union Carbide (U.S.A.). Carboxylic and naphthenic acids are marketed by Shell Chemicals and have been used in extraction processes [87-92]. Amines and quaternary amine salts form another important class of organic extractants for the recovery of metal values from solutions. A lot of important applications [93-100] have been reported in the literature. The amines used commonly have been designated by names such as Alamine 304; Alamine 204; LA-2; Primene-JMR, Adogen 363, 364, 368; Aliquat 336; etc. Tri-n-Butyl phosphate (TBP) and methyl isobutyl ketone (MIK) are two other products which have found use in extraction processes. TBP has seen considerable use in the nuclear industry for the separation of nuclear species [101]. It has also been used successfully for the separation of zirconium and hafnium [102] and for the separation of uranium from impurities before the production of high-grade UO_2 and UO_3 [103]. While Low [104] has pointed out other uses for TBP, Higbie and Hunter [105] have dealt with uses of MIK for the extraction of metals from solutions.

The recovery of copper by solvent extraction using LIX reagents has been so rapid that little attention was given to the kinetics of the extraction reaction for the first few years. Main stress had been on the product development and engineering aspects of the problem. However, certain kinetic studies have been made lately to establish the stoichiometry and the factors affecting the rate of transfer of copper ions from aqueous to the organic phase. Thus Flett *et al.* [106] published such a study which was made by using an AKUFVE apparatus [107]. The rate equation and the reaction kinetics proposed by Flett *et al.* have been discussed by Miller and Atwood [108] who have derived the rate equation using a similar apparatus and radioactive copper tracer. In another study Atwood *et al.* [109] have shown the extraction rate using LIX 64 N, to be

$$\text{Rate} = K [Cu^{2+}]_{aq} [R^{63}H]^{1/2}_{org} [R^{65}H]^{1/2}_{org}$$

$$[H^+]^0_{aq} [R_2^{65}Cu]^0_{org}$$

(LIX 64 N being a mixture of LIX 65 N and LIX 63, the latter acting as a catalyst for the extraction reaction). Whewell *et al.* [110] have also made a kinetic study using LIX 64 N and a single drop method. The dependence of rate reaction on surface area has been shown and the factors affecting the forward and back reactions have been pinpointed.

CONCLUSION

From a survey of the relevant literature and what we have reviewed here, it is not difficult to conclude that the most important recurring cost factor in cementation is the iron scrap. Although copper is still being produced by this method in countries where scrap is easily and abundantly available at reasonable prices, the trend has been in favour of liquid-liquid extraction from the late sixties. In a country like Pakistan where metallic iron is not yet produced locally, the cost of iron scrap may be prohibitive. On the other hand the cost of organic extractants itself is important when viewed from the quantities involved and the losses (although small) entrained during plant operation. Also these extractants are known to be toxic although the extent of toxicity for human and other living organisms is not yet definitely known.

In the meantime other methods of extraction like gaseous reduction, ion exchange and direct electrolysis of leach solutions have made important strides forward. We will deal with them in second part of this review.

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